

# Effect of a Zn impurity on $T_c$ and its implication to pairing symmetry in $\text{LaFeAsO}_{1-x}\text{F}_x$

Yuke Li<sup>1</sup>, Jun Tong<sup>1</sup>, Qian Tao<sup>1</sup>, Chunmu Feng<sup>1</sup>, Guanghan Cao<sup>1,2</sup>, Weiqiang Chen<sup>3</sup>, Fu-chun Zhang<sup>3</sup>, Zhu-an Xu<sup>1,2</sup>†

<sup>1</sup> Department of Physics, Zhejiang University, Hangzhou 310027, China

<sup>2</sup> State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

<sup>3</sup> Department of Physics and Center of Theoretical and Computational Physics, The University of Hong Kong, Hong Kong, China

**Abstract.** The effect of non-magnetic Zn impurity on superconductivity in  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{1-x}\text{F}_x$  system is studied systematically. In the presence of Zn impurity, the superconducting transition temperature increases in the under-doped regime, remains unchanged in the optimally doped regime, and is severely suppressed in the over-doped regime. Our results suggest a switch of the symmetry of the superconducting order parameters from a  $s$ -wave to  $s_{\pm}$  or  $d$ -wave states as the charge carrier doping increases in FeAs-based superconductors.

PACS numbers: 74.70.Dd; 74.20.Rp; 74.62.Dh

† Electronic address: zhuan@zju.edu.cn

## 1. Introduction

Discovery of iron-based superconductivity [1] has generated great interest in condensed-matter physics. Similar to the high transition temperature superconducting (SC) copper oxides, the parent compounds of the iron pnictide are antiferromagnet. Superconductivity emerges upon chemical doping, which introduces charge carriers and suppresses the antiferromagnetic (AFM) order. It is generally agreed that magnetism plays an important role in the superconductivity of both cuprates and pnictides. On the other hand, iron-based superconductors also show different behaviors from the cuprates. One of their major differences is the pairing symmetry. It has been well established that the SC pairing in cuprate is of nodal  $d$ -wave symmetry[2, 3]. In pnictides, the pairing symmetry continues to be an important and outstanding issue. There are clear experimental evidences for full SC gaps in FeAs-based superconductors[4, 5]. Within the full gap scenario, because of the multi Fermi surfaces[6], the relative phases of the SC order parameters in hole or electron pockets can be either positive ( $s$ -wave pairing) or negative ( $s_{\pm}$ -pairing)[7, 8, 9, 10, 11, 12], depending on the sign of the inter-Fermi pocket pair scattering amplitude or their Josephson coupling. The  $s_{\pm}$  pairing is appealing with some experimental supports [13]. In addition, there are also evidences for  $d$ -wave SC gap in FeP-based superconductors[14].

Non-magnetic impurity is an important probe to pairing symmetry. Non-magnetic impurities do not cause severe pair-breaking effect in a conventional  $s$ -wave superconductor according to the Anderson's theorem[15]. In the  $s_{\pm}$  state, the order parameters in hole and electron pockets have opposite signs, non-magnetic impurities like Zn can severely suppress the SC transition temperature  $T_c$ , similar to the effect in high- $T_c$  cuprates with  $d$ -wave pairing[16, 17].

Zinc element has a stable  $d^{10}$  configuration in the alloy [18], and can serve as the best non-magnetic impurity for this study. However, there is a seemingly discrepancy between our early data in  $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$ , where  $T_c$  is essentially unaffected by Zn-impurity[19], and a following report showed a severe suppression of  $T_c$  due to Zn-impurity in the oxygen-deficient  $\text{LaFeAsO}_{1-\delta}$  samples[20]. In this Letter, we report a systematic study of the effect of Zn-impurity on superconductivity in  $\text{LaFeAsO}_{1-x}\text{F}_x$  in different doping regimes. We have observed strong doping dependence of the Zn-impurity effect on  $T_c$ .  $T_c$  is enhanced in the underdoped regime ( $x = 0.05$ ), remains essentially unchanged at the optimal doping ( $x = 0.10$ ), and is severely suppressed at the overdoped regime ( $x = 0.15$ ). Our results suggest a switch of the symmetry of the SC order parameters from a  $s$ -wave to  $s_{\pm}$  or  $d$ -wave states as the charge carrier increases in FeAs-based superconductors. The increase in  $T_c$  at low electron doping may be explained as a result of the suppression of the magnetism upon Zn-doping, which is in favor of the superconductivity.

## 2. Experimental

Polycrystalline samples of  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{1-x}\text{F}_x$  ( $x = 0.05, y = 0, 0.02, 0.04, 0.06$ ;  $x = 0.15, y = 0, 0.02$ ) were synthesized by solid state reaction method. Details on the sample preparation can be found in the previous report[19]. The phase purity of the samples was investigated by powder X-ray diffraction (XRD) using a D/Max-rA diffractometer with  $\text{Cu-K}_\alpha$  radiation and a graphite monochromator. Lattice parameters were calculated by a least-squares fit using at least 20 XRD peaks. Chemical analysis by energy-dispersive x-ray (EDX) microanalysis was performed on an EDAX GENESIS 4000 x-ray analysis system affiliated to a scanning electron microscope (SEM, model SIRION).

The electrical resistivity was measured on bar-shaped samples using a standard four-probe method. The measurements of resistance and Hall effect were performed on a Quantum Design Physical Property Measurement System (PPMS-9). DC magnetization were measured on a Quantum Design Magnetic Property Measurement System (MPMS-5).

## 3. Results and discussion

Figure 1 shows characterization of  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{1-x}\text{F}_x$  samples by the XRD experiments. The inset shows the variations of lattice constants with Zn content for both F-underdoped and F-overdoped samples. All the XRD peaks can be well indexed with the tetragonal  $\text{ZrCuSiAs}$ -type structure, indicating that all the samples are single phase without foreign phases. The  $a$ -axis shrinks slightly with the Zn doping, while the  $c$ -axis increases, similar to the previous report[19]. The EDX measurements found that the actual Zn content ( $x$ ) is very close to the nominal composition, and the variation of Zn content in the samples is less than 5%. These results indicate that Zn has successfully substituted Fe.

Figure 2 shows the temperature dependence of resistivity ( $\rho$ ) for  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{1-x}\text{F}_x$  from 2 K to 300 K and the inset shows the temperature dependence of DC susceptibility for the same samples. For the zinc-free  $\text{LaFeAsO}_{0.95}\text{F}_{0.05}$  sample, the resistivity shows a SC transition at 16.8 K (defined as the midpoint), consistent with the previous report[21]. In the underdoped regime, as shown in Fig.2(a), with the increase of Zn content, to our surprise,  $T_c$  increases to 19.2 K and 22.7 K for  $y = 0.02$  and 0.06 respectively. The  $T_c$  values determined from the magnetic susceptibility exhibits consistent variation with resistivity data. The estimated Meissner volume fraction indicates bulk nature for the superconductivity. Obviously, the above result is in contrast to the case of Zn-doped high- $T_c$  cuprates[22] where  $T_c$  always decreases sharply with Zn doping.

The resistivity and DC susceptibility of overdoped  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{0.85}\text{F}_{0.15}$  ( $y = 0$  and 0.02) samples were shown in Fig. 2 (b). Without Zn doping,  $T_c$  (midpoint) is about 9.6 K. With only 2% Zn doping,  $T_c$  is severely suppressed to below 2 K. We did not observe the diamagnetism in susceptibility in this sample, consistent with the resistivity measurement. These results are in contrast to the case of underdoped

$\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{0.95}\text{F}_{0.05}$  sample and indicate that Zn doping in overdoped region does sharply suppress superconductivity. A similar sharp suppression of  $T_c$  with Zn doping was also reported in the oxygen-deficient  $\text{LaFeAsO}_{1-\delta}$  where the sample is apparently overdoped according to the oxygen content[20].

Fig. 3 shows temperature dependence of Hall coefficient  $R_H$  for  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{1-x}\text{F}_x$  samples. For all the samples, the negative  $R_H$  signal indicates that electron-type charge carrier is dominant in the whole temperature region. For the underdoped  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{0.95}\text{F}_{0.05}$  samples,  $R_H$  of the Zn-free sample exhibits a strong  $T$ -dependence and drops sharply below 100 K, which may be attributed to the residual spin-density-wave (SDW) order or fluctuations.  $R_H$  finally goes to zero as the samples enter into superconducting state. In the parent compound  $\text{LaFeAsO}$ ,  $R_H$  drops sharply due to opening of SDW gap below the structural/magnetic transition temperature [23]. With increasing Zn content, the sharp drop in  $R_H$  is gradually suppressed, indicating that the residual SDW order or fluctuations are further suppressed by Zn impurities. Such an effect of Zn impurities on the SDW order has also been observed in the parent compound  $\text{LaFeAsO}$  [19]. Meanwhile, the room-temperature  $R_H$  remains almost unchanged with Zn doping, indicating that Zn doping does not change the charge carrier density. This is consistent with the band calculation result which predicts that Zn 3d electrons are deep below the Fermi level[18]. For the overdoped  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{0.85}\text{F}_{0.15}$  samples [Fig.3 (b)],  $R_H$  of both the Zn-free and 2% Zn-doped samples exhibit very weak  $T$ -dependence and again the change in the room-temperature  $R_H$  is very small, indicating that the charge carrier density essentially does not change with Zn doping. It should be noted that  $R_H$  drops quickly due to SC transition for the Zn-free sample while it remains constant for Zn-doped sample as  $T$  goes to zero.

The effect of Zn-impurity in the different doping levels is summarized in a phase diagram of  $T_c$  versus Zn content, as shown in Fig. 4. In the underdoped regime, i.e. 5% F doped samples,  $T_c$  remarkably increases with increasing Zn-doped concentration, while in the nearly optimally-doped regime,  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{0.9}\text{F}_{0.1}$ ,  $T_c$  almost does not change with Zn doping, or it is even enhanced slightly at low Zn content. In the overdoped regime, i.e.,  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{0.85}\text{F}_{0.15}$ ,  $T_c$  sharply decreases to below 2 K even with only 2% Zn doping.

Recently the Zn doping effect has also been studied in the hole-type pnictide superconductor  $(\text{Ba,K})\text{Fe}_2\text{As}_2$  [24]. Wen and his collaborators[24] confirmed that superconductivity is robust against the non-magnetic Zn doping in the nearly optimally-doped  $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ , consistent with our result in the optimally doped regime. Meanwhile, a severe suppression of  $T_c$  was reported in a oxygen-deficient 1111 phase  $\text{LaFe}_{1-x}\text{Zn}_x\text{AsO}_{0.85}$  which is apparently overdoped according to the oxygen content [20], in agreement with our result in the overdoped regime. It should also be noted that the partial substitution of other transition metal elements such as Co, Ni, Ru, Rh, Pd, and Ir, not only have negligible pair-breaking effect, but even can induce superconductivity. The 3d electrons of these ions (such as Co, Ni, and Ru) are believed to be itinerant according to the first principle calculations [25]. In contrast, the 3d electrons of Zn ions

are localized without any local moments [18].

Since the impurity effect is very sensitive to the symmetry of the SC order parameter, the contrastive difference in the Zn impurity effect between the underdoped and overdoped regimes cannot easily be explained within the same pairing symmetry state. Instead, our result strongly suggests a switch of the pairing symmetry from an impurity-insensitive pairing state to an impurity-sensitive pairing state. Since other experimental results such as the angle-resolved photoemission spectroscopy (ARPES) measurements [5] have found that the underdoped or optimally doped FeAs-based superconductors should have full superconducting gaps, our present data suggests a  $s$ -wave pairing in the underdoped and optimally doped regime. Meanwhile  $s_{\pm}$  or  $d$ -wave pairings are strongly suggested in the overdoped regime. Iron-based SC compounds have hole Fermi pockets centered at the  $\Gamma$  point in the Brillouin zone and electron pockets centered at the zone corner (M point). The  $s$ -wave and  $s_{\pm}$ -wave states correspond to the same and opposite signs of the relative order parameters between the hole and electron Fermi pockets, which is determined by the sign of the Josephson coupling between the Fermi pockets. A switch from the  $s$ -wave to  $s_{\pm}$  wave states is in accordance to the sign change of the Josephson coupling from attractive at the underdoped to repulsive at over-doped regimes.

Below we shall further elaborate the scenario of a switch between pairing states. The impurity effect in the  $s_{\pm}$ -wave state was studied by Bang et al.[16] and by Onari and Kontani[17]. Theoretical calculations have shown that in the strong scattering limit the non-magnetic impurity effect to  $s_{\pm}$ -wave state is severe and similar to the effect on  $d$ -wave SC state[16]. Their theory should apply to Zn-impurity located in the Fe-planes, where the scattering is strong. The severe suppression of  $T_c$  in the overdoped regime may thus be well explained within the scenario of  $s_{\pm}$ -wave symmetry. Moreover, the  $d$ -wave pairing is unlikely according to the ARPES studies in the overdoped regimes [26, 27]. On the other hand, the insensitivity of the impurity effect in the underdoped and optimally doped regimes is not compatible with the  $s_{\pm}$  pairing. Note that the suppression of  $T_c$  by impurities in the  $s_{\pm}$  wave is not dependent on the charge carrier doping level. Our data strongly suggest that in the underdoped and optimally doped regime, the SC pairing is likely  $s$ -wave, essentially unaffected by the Zn-impurity according to Anderson theorem[15]. The enhancement of  $T_c$  with Zn-impurity in the underdoped regime may be explained as the result of the suppression of AFM order, which in turn enhances superconductivity.

We remark that the possible changes in pairing symmetry with doping level were also proposed in a recent NMR study on the P-doped  $\text{BaFe}_2\text{As}_2$  system [28], and in a theoretical proposal for time reversal symmetry breaking state[29], and in a theory for a possible switch between nodeless and nodal pairings by changing the pnictogen height measured from the Fe plane [30].

#### 4. Conclusion

In summary, we have studied systematically the effect of non-magnetic Zn-impurity on superconductivity in various doping regimes of  $\text{LaFeAsO}_{1-x}\text{F}_x$  systems. The Zn-impurities do not suppress superconductivity in the underdoped and optimally doped regimes, but severely suppress superconductivity in the overdoped regime. Our results suggest a switch of the pairing symmetry from Zn-impurity insensitive  $s$ -wave at underdoped and optimally doped regime to impurity-sensitive pairing state (likely  $s_{\pm}$ -wave) at overdoped regime. The enhancement in  $T_c$  with increasing Zn content at the low F-doping regime could result from the suppression of AFM order or fluctuation in FeAs layers which competes with superconductivity.

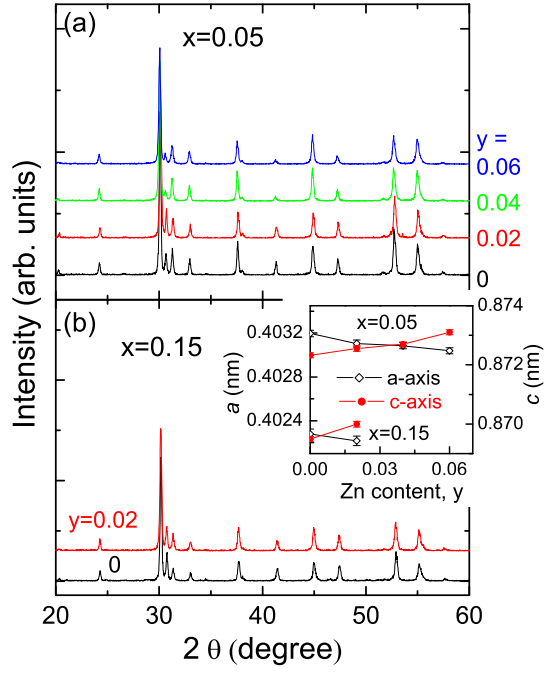
#### Acknowledgments

This work is supported by the National Science Foundation of China (Grant nos 10634030 and 10931160425), PCSIRT (IRT-0754), the National Basic Research Program of China (Grant No. 2007CB925001). We also acknowledge partial support from Hong Kong RGC grant HKU 7068/09P and NSF/RGC N-HKU 726/09.

#### References

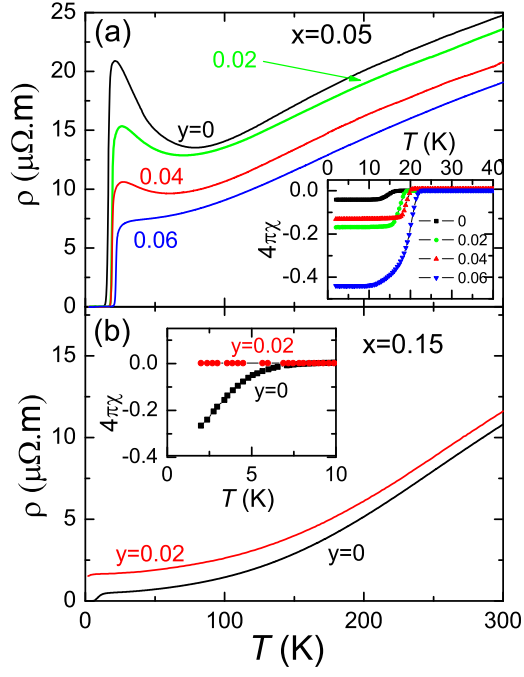
- [1] Kamihara Y, Watanabe T, Hirano M, and Hosono H 2006 *J. Am. Chem. Soc.* **130** 3296
- [2] Tsuei C C, Kirtley J R, Chi C C 1994 *Phys. Rev. Lett.* **73** 593
- [3] Wollman D A, Van Harlingen D J, Lee W C, Ginsberg D M, and Leggett A J 1993 *Phys. Rev. Lett.* **71** 2134
- [4] Chen T Y, Tesanovic Z, Liu R H, Chen X H, and Chien C L 2008 *Nature (London)* **453** 1224
- [5] Ding H, Richard P, Nakayama K, Sugawara K, Arakane T, Sekiba Y, Takayama A, Souma S, Sato T, Takahashi T, Wang Z, Dai X, Fang Z, Chen G F, Luo J L, and Wang N L 2008 *Europhys. Lett.* **83** 47001
- [6] Singh D J and Du M H 2008 *Phys. Rev. Lett.* **100** 237003
- [7] Mazin I I, Singh D J, Johannes M D, and Du M H 2008 *Phys. Rev. Lett.* **101** 057003
- [8] Kuroki K, Onari S, Arita R, Usui H, Tanaka Y, Kontani H, and Aoki H 2008 *Phys. Rev. Lett.* **101** 087004
- [9] Seo K, Bernevig B A, Hu J 2008 *Phys. Rev. Lett.* **101** 206404
- [10] Cvetkovic V, Tesanovic Z 2009 *Europhys. Lett.* **85** 37002
- [11] Wang F, Zhai H, Ran Y, Vishwanath A, and Lee D H 2009 *Phys. Rev. Lett.* **102** 047005
- [12] Chen W Q, Yang K Y, Zhou Y, and Zhang F C 2009 *Phys. Rev. Lett.* **102** 047006
- [13] Chen C T, Tsuei C C, Ketchen M B, Ren Z A, and Zhao Z X 2010 *Nature Physics* **6** 260
- [14] Hicks C W, Lippman T M, Huber M E, Analytis J G, Chu J H, Erickson A S, Fisher I R, and Moler K A 2009 *Phys. Rev. Lett.* **103** 127003
- [15] Anderson P W 1959 *J. Phys. Chem. Solids* **11** 26
- [16] Bang Y, Choi H, and Won H 2009 *Phys. Rev. B* **79** 054529
- [17] Onari S, and Kontani H 2009 *Phys. Rev. Lett.* **103** 177001
- [18] Zhang L J, and Singh D J 2009 *Phys. Rev. B* **80** 214530
- [19] Li Y K, Lin X, Tao Q, Wang C, Zhou T, Li L J, Wang Q B, He M, Cao G H, and Xu Z A 2009 *New J. Phys.* **11** 053008

- [20] Guo Y F, Shi Y G, Yu S, Belik A A, Matsushita Y, Tanaka M, Katsuya Y, Kobayashi K, Nowik I, Felner I, Awana V P S, Yamaura K, and Muromachi E T 2009 arXiv: 0911.2975.
- [21] Luetkens H, Klauss H H, Kraken M, Litterst F J, Dellmann T, Klingeler R, Hess C, Khasanov R, Amato A, Baines C, Kosmala M, Schumann O J, Braden M, Borrero J H, Leps N, Kondrat A, Behr G, Werner J, and Buchner B 2009 *Nat. Mater.* **8** 305
- [22] Xiao G, Cieplak M Z, Gavrin A, Streita F H, Bakhshai A, and Chien C L 1988 *Phys. Rev. Lett.* **60** 1446
- [23] McGuire M A, Christianson A D, Sefat A S, Sales B C, Lumsden M D, Jin R, Payzant E A, Mandrus D, Luan Y, Keppens V, Varadarajan V, Brill J W, Hermann R P, Sougrati M T, Grandjean F, and Long G J 2008 *Phys. Rev. B* **78** 094517
- [24] Cheng P, Shen B, Hu J P, and Wen H H 2010 *Phys. Rev. B* **81** 174529
- [25] Xu G, Ming W, Yao Y, Dai X, Zhang S C, and Fang Z 2008 *Europhys. Lett.* **82** 67002
- [26] Terashima K, Sekiba Y, Bowen J H, Nakayama K, Kawahara T, Sato T, Richard P, Xu M Y, Li L J, Cao G H, Xu Z A, Ding H, and Takahashi T 2009 *PNAS* **106** 7330
- [27] Sekiba Y, Sato T, Nakayama K, Terashima K, Richard P, Bowen J H, Ding H, Xu Y M, Li L J, Cao G H, Xu Z A, and Takahashi T 2009 *New J. Phys.* **11** 025020
- [28] Nakai Y, Iye T, Kitagawa S, Ishida K, Kasahara S, Shibauchi T, Matsuda Y, and Terashima T 2010 *Phys. Rev. B* **81** 020503(R)
- [29] Lee W C, Zhang S C, and Wu C J 2009 *Phys. Rev. Lett.* **102** 217002
- [30] Kuroki K, Usui H, Onari S, Arita R, and Aoki H 2009 *Phys. Rev. B* **79** 224511

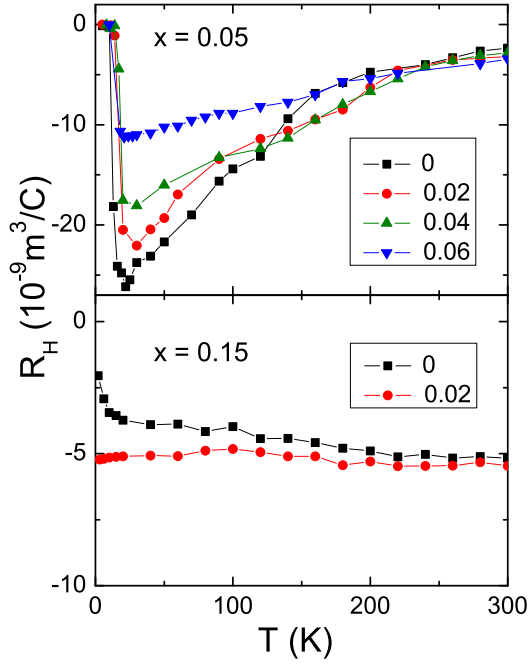


**Figure 1.** (color online). Structural characterization of  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{1-x}\text{F}_x$  samples. (a) and (b) Powder X-ray diffraction patterns for  $x=0.05$  and  $0.15$ , respectively. Inset: Lattice parameters as functions of Zn content.

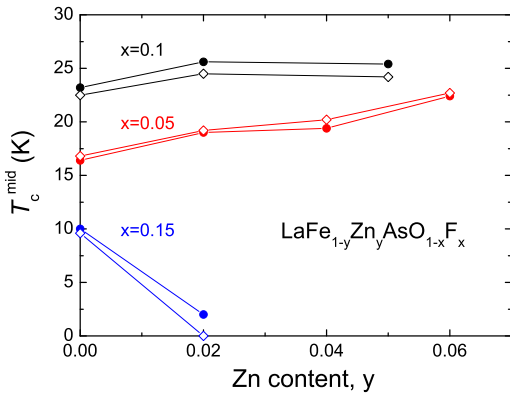




**Figure 2.** (color online). Temperature dependence of resistivity ( $\rho$ ) for the  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{1-x}\text{F}_x$  samples. The inset: diamagnetic transitions under a magnetic field of 10 Oe with field-cooling (FC) mode. (a)  $x = 0.05$ ,  $y = 0, 0.02, 0.04$ , and  $0.06$ ; (b)  $x = 0.15$ ;  $y = 0$  and  $0.02$ .



**Figure 3.** (color online) Temperature dependence of Hall coefficient  $R_H$  measured at 5 T for  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{1-x}\text{F}_x$ . (a)  $x = 0.05$ ,  $y = 0, 0.02, 0.04, 0.06$ ; (b)  $x = 0.15$ ,  $y = 0, 0.02$ .



**Figure 4.** (color online) Superconducting transition temperatures versus Zn content in  $\text{LaFe}_{1-y}\text{Zn}_y\text{AsO}_{1-x}\text{F}_x$ . Solid and open symbols refer to  $T_c$  determined from the measurements of resistivity (midpoint) and susceptibility (onset point), respectively. The data of  $x = 0.1$  were taken from the previous report.[19]